REMARKS

The present response amends claims 1 and 9, adds new claim 10, cancels claims 2 and 4 without prejudice and requests reconsideration of the rejected claims.

The bases for amending claim 1 and adding claim 10 can be found at page 4, line 12, plus page 5, lines 4-6, where it is stated that the binder can be a silica sol, or a silica sol blended with an alkali metal silicate. The silica sol has silica particles with sizes equal to or smaller than 10 nm, see page 4, line 20. Further basis is present at page 4, lines 22-24, where it is stated that the SiO_2/M_2O mole ratio of a silica sol binder preferably is at least 25:1. And from page 5, lines 7-11, is clear that the SiO_2/M_2O mole ratio of a blend of a silica sol and an alkali metal silicate preferably is above 15:1. Basis for the zinc component can be found in original claim 4.

Claims 1-9 are rejected under 35 U.S.C. 102(b) as allegedly being anticipated by or, in the alternative, under 35 U.S.C. 103(a) as allegedly being obvious over van der Kolk et al. '056, Schutt '824 or '784, Tanaka et al '536 B1, Campbell '224, Yoshida et al. '030, Beers '864, McLeod '096,. Karchevsky et al. '036 B1 or '059 B1, Cuneo '039, Weldes '194, McMahon '061, Patton '746, NL 6604385 (DuPont-abstract), JP 51073029 (Ito et al.), JP 51079125 (Ito et al.), or JP 51150533 (Matsui et al.). Each of these rejections is traversed, in turn, below.

US 4,888,056 Van der Kolk

This document relates to shop primers comprising a silicate-type binder. The use of a silica sol or a mixture of a silicate solution with a silica sol is not mentioned or suggested. Consequently, amended claims 1 and 9, new claim 10, and claims 2-8, which depend from claim 1, are not anticipated by Van der Kolk '056.

There is no suggestion or expressed expectation of success in Van der Kolk that would have led one to add a silica sol to the system of Van der Kolk, let alone the use of a silica sol having a SiO_2/M_2O mole ratio of at least 15:1 or 25:1 and an average particle size equal to or smaller than 10 nm. Hence, the subject matter of

amended claims 1 and 9, new claim 10, and claims 2-8, which depend from claim 1, are not obvious based on Van der Kolk.

US 4,479,824 Schutt

This document relates to coating compositions comprising an alkali metal silicate based binder. A silica gel is added to a silicate solution after which the mixture is blended, see column 3, lines 54-66. The gel used consists of micron size lumps, see column 6, lines 48-50. The gel at least partially dissolves in the original silicate solution, see column 3, lines 54-66.

Optionally a silica sol is added to increase the SiO_2/M_2O mole ratio of said binder to a value of 5.5:1 to 6.5:1, see column 4, lines 48 and 49. A binder having a SiO_2/M_2O mole ratio of at least 15:1 or 25:1 is not disclosed. The sols added to the silicate solution are micron-sized, see column 10, claim 5. Hence, amended claims 1 and 9, new claim 10, and claims 2-8, which depend from claim 1, are not anticipated by Schutt '824.

There is no suggestion or expressed expectation of success in Schutt that would have led one to add a silica sol having a SiO_2/M_2O mole ratio of at least 15:1 or 25:1 and an average particle size equal to or smaller than 10 nm. Hence, the subject matter of amended claims 1 and 9, new claim 10, and claims 2-8, which depend from claim 1, are not obvious based on Schutt '824.

US 3,620,784 Schutt

This document relates to coating compositions comprising a potassium silicate-type binder. The SiO_2/K_2O mole ratio of said binder preferably is in the range of 4.8:1 to 5.3:1, see column 1, lines 54-59. The use of a silica sol or a mixture of a silicate solution with a silica sol is not mentioned or suggested. Consequently, amended claims 1 and 9, new claim 10, and claims 2-8, which depend from claim 1, are not anticipated by Schutt '784.

There is no suggestion or expressed expectation of success in Schutt that would have led one to add a silica sol to the system of Schutt, let alone the use of a silica sol having a SiO_2/M_2O mole ratio of at least 15:1 or 25:1 and an average particle size equal to or smaller than 10 nm. Hence, the subject matter of amended claims 1 and 9, new claim 10, and claims 2-8, which depend from claim 1, are not obvious based on Schutt '784.

US 6,482,536 Tanaka

This document relates to coating compositions comprising a film-forming resin and silica particles. The silica particles are used as a matting agent, see column 1, lines 54-59. Hence, the silica added is not a silica sol based binder or a binder comprising a mixture of a silica sol and a silicate. Rather, it is a pigment. Moreover, the average particle size of the silica particles added is in the range of 0.5 to 15 μm, i.e. 500 to 15000 nm. Hence, amended claims 1 and 9, new claim 10, and claims 2-8, which depend from claim 1, are not anticipated by Tanaka '536.

There is no suggestion or expressed expectation of success in Tanaka that would have led one to add a silica sol to the system of Tananka, let alone the use of a silica sol having a SiO_2/M_2O mole ratio of at least 15:1 and an average particle size equal to or smaller than 10 nm. Hence, the subject matter of amended claims 1 and 9, new claim 10, and claims 2-8, which depend from claim 1, are not obvious based on Tanaka '536.

US 3,715,224 Campbell

This document describes compositions comprising solutions or colloidal suspensions of silicate compounds with a specified SiO_2/RO ratio and/or SiO_2/R_2O ratio. R stands for Cu, Ag, Cd, Sr, Ca, Ba, Co, Pb, Mg, Ni, Zn, or Mn, see column 3, lines 1 and 2. Thus, R does not stand for ammonium or an alkali metal, i.e. Li, Na, K, Rb, or Cs. From the document is not clear whether the colloidal suspensions are sol systems or polysilicates. The size of the colloids is not revealed.

Optionally, NH_4OH, $LiOH$, KOH, $NaOH$ and an alkali metal or ammonium silicate can be added to the RO silicate compounds, see column 2, lines 51-56, and column 3, lines 57-67. The alkali metal silicates and the ammonium silicate used in the examples are silicate solutions and polysilicates, not silica sols.

Whether the ammonium or alkali metals clamp onto the RO and R_2O silica colloids is not clear. Nevertheless, Campbell does not disclose a binder comprising a silica sol having a SiO_2/M_2O mole ratio of at least 15:1 or at least 25:1 and an average particle size equal to or smaller than 10 nm. Moreover, Campbell does not disclose a coating composition comprising zinc powder and/or a zinc alloy. (R may be Zn, but that indicates that Zn ions can be present in the colloidal suspensions; that is not the same as zinc powder and/or a zinc alloy.) Hence, amended claims 1 and 9, new claim 10, and claims 2-8, which depend from claim 1, are not anticipated by Campbell '224.

There is no suggestion or expressed expectation of success in Campbell that would have led one to make a binder comprising zinc powder and/or a zinc alloy and a silica sol having a SiO_2/M_2O mole ratio of at least 15:1 or 25:1 and an average particle size equal to or smaller than 10 nm. Hence, the subject matter of amended claims 1 and 9, new claim 10, and claims 2-8, which depend from claim 1, are not obvious based on Campbell '224.

US 4,006,030 Yoshida

This document relates to coating compositions comprising a silica sol or silicate solution. The compositions may comprise a silica sol having a particle diameter of less than 5 mμ (milli-micron), i.e. less than 5 nm. Alternatively, the silica sol has particle sizes between 5 and 300 nm. The coating compositions of Yoshida are suitable to coat surfaces of cured inorganic substrates, particularly cement. At column 3, lines 62-68, it is mentioned that a pigment may be present in the coating composition. This document does not disclose coating compositions comprising zinc powder or a zinc alloy. Hence, amended claims 1 and 9, new claim 10, and claims 2-8, which depend from claim 1, are not anticipated by Yoshida '030.

There is no suggestion or expressed expectation of success in Yoshida that would have led one to use the composition for the coating of metal substrates. Hence, the subject matter of amended claims 1 and 9, new claim 10, and claims 2-8, which depend from claim 1, are not obvious based on Yoshida '030 for these reasons as well as for the reasons why the claims are not anticipated based on this reference.

US 3,893,864 Beers

This document relates to the preparation of coating compositions by combining a silicate solution or a colloidal silica with the proper ratio of a colloidal silica sol, which sol is stabilised with a fugitive cation, especially NH_4^+ (NH_3 evaporates easily). See column 3, lines 39-46. When this combination is made, an immediate reaction occurs, which results in a high molecular weight polysiloxane having a large particle size compared to silicate solutions or sols, see column 6, lines 4-12. The particle size of the ammonium (or ammonia, this is interchangeable for aqueous systems) stabilised silica sols used is not mentioned in the description, but in the examples Ludox AS is used, which is NH_3 stabilised and has a particle size of 22 nm. Beers does not disclose a binder comprising a silica sol having a SiO_2/M_2O mole ratio of at least 15:1 or 25:1 and an average particle size equal to or smaller than 10 nm. Hence, amended claims 1 and 9, new claim 10, and claims 2-8, which depend from claim 1, are not anticipated by Beers '864.

There is no suggestion or expressed expectation of success in Beers that would have led one to make a binder comprising a silica sol having a SiO_2/M_2O mole ratio of at least 15:1 or 25:1 and an average particle size equal to or smaller than 10 nm. Hence, the subject matter of amended claims 1 and 9, new claim 10, and claims 2-8, which depend from claim 1, are not obvious based on Beers '864.

US 4,086,096 McLeod

This document relates to solvent·borne coating compositions comprising a polyol silicate. The organic solvent present in the composition is a solvent for the polyol silicate, see column 3, lines 25 + 26. This document does not disclose or

suggest coating compositions comprising an aqueous silica sol. Consequently, amended claims 1 and 9, new claim 10, and claims 2-8, which depend from claim 1, are not anticipated by McLeod '096.

There is no suggestion or expressed expectation of success in McLeod that would have led one to add a silica sol to the system of McLeod, let alone the use of a silica sol having a SiO_2/M_2O mole ratio of at least 15:1 or 25:1 and an average particle size equal to or smaller than 10 nm. Hence, the subject matter of amended claims 1 and 9, new claim 10, and claims 2-8, which depend from claim 1, are not obvious based on McLeod '096.

US 6,337,036 B1 Karchevsky and US 6,329,059 B1 Karchevsky

These documents relate to coating compositions comprising a quaternary ammonium silicate. This is a solution, not a sol. The documents do not disclose or suggest coating compositions comprising a silica sol. Hence, amended claims 1 and 9, new claim 10, and claims 2-8, which depend from claim 1, are not anticipated by Karchevsky '036 B1 or '059 B1.

There is no suggestion or expressed expectation of success in these documents that would have led one to add a silica sol to the system of McLeod, let alone the use of a silica sol having a SiO_2/M_2O mole ratio of at least 15:1 or at least 25:1 and an average particle size equal to or smaller than 10 nm. Hence, the subject matter of amended claims 1 and 9, new claim 10, and claims 2-8, which depend from claim 1, are not obvious based on Karchevsky '036 B1 and/or '059 B1.

US 3,392,039 Cuneo

This document relates to solutions, that can be used in coatings, comprising SiO_2 and Li_2O in a ratio between 1:1 and 8:1. The aim of this study is to prepare crystalloidal silicate solutions instead of sol comprising mixtures, see column 1, lines 65-70, and column 2, lines 30-38. This is confirmed by Iller, Chapter 2, page 148, paragraphs 2 and 3 (enclosed herewith). Hence, amended claims 1 and 9, new

claim 10, and claims 2-8, which depend from claim 1, are not anticipated by Cuneo '039.

There is no suggestion or expressed expectation of success in Cuneo that would have led one to add a silica sol to the system of Cuneo, let alone the use of a silica sol having a SiO_2/M_2O mole ratio of at least 15:1 or 25:1 and an average particle size equal to or smaller than 10 nm. Hence, the subject matter of amended claims 1 and 9, new claim 10, and claims 2-8, which depend from claim 1, are not obvious based on Cuneo '039.

US 3,345,194 Weldes

This document relates to coating compositions comprising a solution of organic ammonium silicates. The documents do not disclose or suggest coating compositions comprising a silica sol. Hence, amended claims 1 and 9, new claim 10, and claims 2-8, which depend from claim 1, are not anticipated by Weldes '194.

There is no suggestion or expressed expectation of success in Weldes that would have led one to add a silica sol to the system of Weldes, let alone the use of a silica sol having a SiO_2/M_2O mole ratio of at least 15:1 or 25:1 and an average particle size equal to or smaller than 10 nm. Hence, the subject matter of amended claims 1 and 9, new claim 10, and claims 2-8, which depend from claim 1, are not obvious based on Weldes '194.

US 3,130,061 McMahon

This document relates to coating compositions that are prepared by either adding alkali stabilised colloidal silica to an "aqueous colloidal lithium silicate solution" (column 2, lines 58-66), or by mixing an aqueous lithium hydroxide solution and colloidal silica sol (column 2, lines 49-57). The molecular ratio of lithium oxide to silica is at least 1:40 and up to 1:2.5, see column 5, lines 69-74.

The method described by McMahon is a standard way of producing lithium polysilicates, see Iller, Chapter 2, page 148 (enclosed herewith). McMahon states at

column 8, lines 15-18, that after the addition of lithium hydroxide to collodial silica sol the components react to form a soft gel. Reading Iller, this gel must be a polysilicate. Hence, McMahon does not disclose a binder comprising a sol. Thus, amended claims 1 and 9, new claim 10, and claims 2-8, which depend from claim 1, are not anticipated by McMahon '061.

At column 8, lines 28-29, McMahon states that if the lithium hydroxide content is too low, the collodial nature of the silica will be exaggerated. McMahon thus teaches away from using a sol system as a binder; he teaches to use the reaction product of lithium hydroxide with colloidal silica sol, i.e. a polysilicate. McMahon does not disclose a coating composition comprising a silica sol having a SiO_2/M_2O mole ratio of at least 15:1 or 25:1 and an average particle size equal to or smaller than 10 nm. Hence, the subject matter of amended claims 1 and 9, new claim 10, and claims 2-8, which depend from claim 1, are not obvious based on McMahon '061.

US 3,180,746 Patton

This document relates to the preparation of coating compositions comprising a lithium-sodium silicate solution. See also Iller, Chapter 2, page 148 (enclosed herewith). This document does not disclose or suggest coating compositions comprising an aqueous silica sol. Consequently, amended claims 1 and 9, new claim 10, and claims 2-8, which depend from claim 1, are not anticipated or made obvious by Patton '746.

NL 6604385 DuPont (abstract)

This document relates to coating compositions comprising a lithium silica binder in which the bigger units act like colloidal SiO_2. The binder has a SiO_2/Li_2O ratio between 4:1 and 25:1, preferably between 5:1 and 7:1. This document does not disclose or suggest coating compositions comprising a silica sol having a SiO_2/M_2O mole ratio of at least 15:1 or 25:1 and an average particle size equal to or smaller than 10 nm. Hence, amended claims 1 and 9, new claim 10, and claims 2-8, which

depend from claim 1, are not anticipated or made obvious by the abstract of NL 6604385.

JP 51073029 Ito (abstract)

This document relates to coating compositions comprising a colloidal SiO_2 dispersion having a SiO_2/Li_2O ratio of 3:1 to 50:1. In the Example in the abstract, the commercial product Snowtex-20 is used. This product comprises silica sols having a particle size above 10 nm, see Iller page 417 (enclosed herewith). The abstract does not mention or suggest compositions comprising silica or silicate particles have an average size equal to or smaller than 10 nm. Accordingly, amended claims 1 and 9, new claim 10, and claims 2-8, which depend from claim 1, are not anticipated or made obvious by JP 51073029 Ito (abstract).

JP 51079125 Ito (abstract)

This document relates to a coating composition prepared from a colloidal silica dispersion. The colloidal silica used in the example is Snowtex-20. This is an alkali stabilised sol dispersion wherein the particle size is above 10 nm. Amine is added to the composition such that the composition has a $SiO_2/amine$ ratio of 10:1 – 1:2. The further composition comprises metals such as Cr, Mo, and W, but no alkali metals. The abstract does not mention or suggest compositions comprising silica or silicate particles have an average size equal to or smaller than 10 nm. Accordingly, amended claims 1 and 9, new claim 10, and claims 2-8, which depend from claim 1, are not anticipated or made obvious by JP 51079125 Ito (abstract)

JP 51150533 Matsui

This document relates to coating compositions comprising an aqueous solution of silicates and colloidal silica. From the abstract it seems that the SiO_2/M_2O ratio of the final composition is not higher than 5:1. Accordingly, amended claims 1 and 9, new claim 10, and claims 2-8, which depend from claim 1, are not anticipated or made obvious by JP 51150533 Matsui

Claims 8 and 9 are rejected under 35 U.S.C. 112, second paragraph, for the recitation "water-based". It is submitted that this recitation complies with the requirements of 35 U.S.C. 112, second paragraph. The skilled artisan understands what is meant by this recitation which has been used in the claims of granted U.S. patents, e.g., 6,506,458 (claim 8) and 6,447,620 (claims 1-3). Accordingly, while the suggestion for amending these claims is appreciated, it has not been adopted because it is not considered necessary and it is desirable to avoid unnecessary amendments to avoid any possible implications from FESTO.

Respectfully submitted,

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Encl: Iller, Chapter 2, pages 145-150, and Iller pages 416-418.

added. However, when parti-
1 by adjusting the ratio to less
e silica is converted to silicate
to be an equilibrium mixture
silica of such extremely small

from sodium and potassium

o of 10:1, for example, is
alkali metal silicate and a
f fireproof coating mixtures

abilized with NaOH around
le more alkali and the lower
, in the ratio range of about
ly found to be unstable, and
solution was added to a
o from 100:1 to 5:1, for
9) found that by aging or
Thus solutions with ratios
pared from sols originally
er heating destabilizes the
pears, the polysilicate solu-
ar und half of the silica is
ity with the molybdic acid
olloid remains as such, but
at equilibrium.
at when it is mixed with a
a along with a sol contain-
there is formed a mixture
ar, hard, adherent, water-
are filled by 7 nm parti-
lloidal component of the
r size by the soluble ionic
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ervious.
ken (90) claimed that by
acid, temporarily stable
ge 4:1 to 6:1, as in Iler's

l have been prepared by
silicate to above 100°C

to cause intumescence, and then the partly dried mass is further heated to 315°C, after which the mass can be dissolved to give a polysilicate solution (91). The higher temperature apparently partly dissolves the agglomerated silica powder, bringing about its disaggregation. Probably the amorphous powder employed must consist of ultimate silica particles of the same size range as in the sols employed in earlier processes. According to a German patent, if waste silicic acid powder from the AlF$_3$ process is used, it is so lightly agglomerated that it can be dispersed by alkali alone to give a solution of 4.3:1 ratio of SiO_2:Na_2O containing 13.7% SiO_2 (92).

Potassium Polysilicate

It has not generally been recognized that in the polysilicate system, the potassium ion behaves very differently from sodium. Although the coagulating effect of these ions is generally similar in most colloid systems and even in colloidal silica at pH 7–10, the potassium loses its coagulating effect at higher pH but sodium does not. (This is discussed in further detail in Chapter 4.)

When concentrated 3.25 ratio sodium silicate is mixed with an alkali-stabilized sol containing 30% silica, coagulation and gelling occur at once, but they do not occur if potassium silicate is added. This is apparently the basis for the disclosure of Waltersdorf (93). Thus stable mixtures of colloidal silica and potassium silicate can be prepared with a silica concentration of 15–30 wt. %, with SiO_2:K_2O molar ratios of 11:1 to 24:1. Although it is not so stated, such compositions are relatively stable toward prolonged heating in comparison with similar sodium based mixtures, which tend to crystallize.

Appreciation of this effect has led to the development of a number of practical applications. Thus amorphous silicic acid powder is heated with 2.4:1 ratio potassium silicate solution to give a viscous solution that forms a binder for a pigmented coating on asbestos-cement board (94). The final molar ratio of SiO_2:K_2O is 5.7:1. A composition with similar use is described by Yano (95).

Another unusual application of the compatibility of potassium silicate with sodium-free colloidal silica is described by Shoup (96). By mixing concentrated potassium silicate solution with a concentrated silica sol and adding an ester, aldehyde, or amide which liberates acid as a homogeneous gelling agent, very strong, dense, uniform silica gels can be made in cast shapes. When washed with acid to remove the potassium salt, these gels are so strong and coherent that they dry in the shape in which they are cast. Because the silica is so concentrated, cracking is minimized as the gel shrinks as it is dried. When fired at 900°C it gives a strong body with 70% by volume porosity. It can then be fired at 1400°C and further shrunk to an object of clear fused silica without losing its relative shape (97).

LITHIUM SILICATES

The lithium ion is very different from sodium or potassium in its behavior in silica systems. The lithium ion resembles these elements to some extent at ordinary

Polysilicate	Type 48	Type 85
SiO$_2$(%)	20	20
Li$_2$O(%)	2.1	1.2
Molar ratio SiO$_2$:Li$_2$O	4.8:1	8.5:1
Viscosity (cps)	12	8
Specific gravity	1.17	1.17
pH	11	11
Shelf-life at 75°F (months)	12	12

temperature but above about 60°C it assumes some of the characteristics of calcium. Thus, although a solution of lithium silicate can be made by dissolving amorphous silica in LiOH solution at 20–40°C, the silicate comes out of solution when heated. The effect is reversible; it is remarkable to see the solution solidify to a white mass when hot, then reliquefy to a clear homogeneous state after being cooled to 25°C for a few hours.

Ordway (57) in 1907 studied the properties of lithium silicate with molar ratios of SiO$_2$:Li$_2$O of 1:1 to 2.3:1 and noted the peculiar reversible insolubility when the solution was heated and cooled. Even as late as 1952, Vail (1) stated that the possible concentrations and ranges of composition of lithium silicate were much more restricted than in the case of sodium. In 1969, Weldes and Lange summarized the properties of available aqueous lithium silicate systems (19).

It is apparently only since 1950 that it has been appreciated that stable solutions of lithium silicates and polysilicates could be prepared with any desired SiO$_2$:Li$_2$O ratio and that these have useful properties.

The difference from sodium is especially apparent in concentrated solutions with molar ratios of SiO$_2$:Li$_2$O from 4:1 to 15:1 or higher. These are clear and quite stable at 25°C whereas, as previously discussed, most of the analogous sodium silicate compositions either gel or crystallize. Furthermore, the properties of concentrated sols of colloidal silica are appreciably different from those stabilized by sodium base, especially in regard to much greater compatibility with water-miscible organic solvents.

Lithium silicate solution cannot be made by dissolving the glass, so is prepared by dissolving very finely divided amorphous silica in LiOH solution at 20–50°C. However, the reaction apparently proceeds more rapidly at 75–250°C in an autoclave, whereby one obtains a solution of LiSiO$_3$ plus a precipitate of higher ratio silicates which dissolves when the solution is aged at 20–30°C (98). A solution of 3.8 molar ratio can be prepared by adding 200 mesh silicon powder to a stirred 12% solution of LiOH·H$_2$O, from which hydrogen is evolved, while the temperature is held at 38–45°C. The slightly viscous filtered solution contained 19% SiO$_2$ (99). Another approach is to prepare a cation-exchange resin in lithium form and pass a solution of sodium silicate through it to exchange sodium for lithium (100).

Lithium Polysilicates

In 1954 it was discovered by Iler (101) that concentrated stable solutions containing SiO$_2$:Li$_2$O molar ratios from 4:1 to 25:1 could be obtained by adding LiOH to a solution of polysilicic acid, to a suspension of silica gel, or to a silica sol free from alkali metal or other cations. Since the mixtures thickened or immediately set to a gel, this approach appeared useless until it was found that after a few hours or a day or so at ordinary temperature, the mass spontaneously liquefied. When such mixtures were heated to 80–100°C to accelerate liquefaction, they remained gelled. The liquid compositions contained both ionic and colloidal silica.

Since compositions of all SiO$_2$:Li$_2$O ratios from 4:1 to 25:1 are soluble and stable, this system offered Iler an opportunity to examine the relation between the silica to alkali ratio and the nature of the colloid species present. Lithium polysilicate solutions were made by mixing solutions of polysilicic acid, obtained by ion exchange from 3.25 ratio sodium silicate, and lithium hydroxide and aging the mixtures at 25°C for a week until clear liquids were obtained at equilibrium. The solutions contained 10% of SiO$_2$ and the SiO$_2$:Li$_2$O ratios ranged from 3:1 to 10:1.

These solutions were compared by measuring the rate of formation of the yellow silicomolybdic acid when microsamples were suddenly mixed with molybdic acid solution at low pH. For each sample, the percent of the total silica, P, which had reacted at time t was noted at 2.5, 5, 10, 15, and 20 min at 25°C. A solution of sodium silicate of 3.3:1.0 M ratio was also included and found to react in about the same way as the lithium silicate solution of corresponding ratio.

It was assumed that the solutions all consisted, for the most part, of monomeric silicate ions and higher molecular weight polysilicate ions in the form of very small charged colloidal particles. Since the monomeric ions react with molybdate in about 2.5 min, the percent of monomeric silica, P_m, was noted in each case.

Then $P - P_m$, or p, was the percent silica in the polymeric state that had reacted at time, t. This was found to follow the equation

$$\log \frac{100 - p}{100} = kt \qquad \text{(see Figure 2.4)}$$

The values of k, the relative reaction rate, were plotted against $(R - 2)^{-1}$ since colloidal species are present only at a ratio greater than 2:1. This gave the relation shown in Figure 2.5. Since, as has been elsewhere noted, the reaction rate is an inverse function of particle size of the colloid, it is concluded that the size of the colloidal species must increase regularly and spontaneously in proportion to the degree to which the ratio exceeds about 2:1. This is at least true in the ratio range 3:1 to 10:1. At higher ratios, the particle size is less closely related to ratio, since it is well
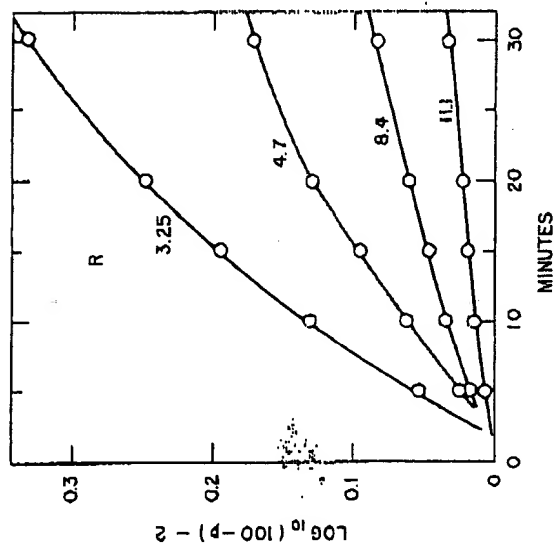
Figure 2.4. Reaction of colloid species of silica in lithium polysilicate solutions of different ratios of SiO_2:Li_2O (indicated on curves) with molybdic acid reagent.

Figure 2.5. Relative rates of reaction of colloid species in lithium polysilicates with molybdic acid reagent versus $(R - 2)^{-1}$, where R is the molar ratio of SiO_2:Li_2O.

known that at ratios higher than 25:1, sols of different particle sizes can be stabilized at the same ratio without much, if any, difference in particle size.

Thus the polysilicate solution spontaneously equilibrates to a mixture of monomeric species and colloidal species, the size of which increases with increasing ratio over 2:1.

Numerous procedures for manufacture have been suggested. Cuneo (103) prepared a lithium polysilicate from a 2.6% silica sol obtained from sodium silicate by ion exchange, by adding LiOH to attain ratios of 2.5:1 to 8:1 and then concentrating the solution by vacuum evaporation to a silica content of 21%. More "crystalloidal," as opposed to colloidal, silica was said to be present because of the nature of the starting sol which probably contained silica particles 1-2 nm in diameter.

A lithium polysilicate solution of 3.5 M ratio can also be made by heating finely divided amorphous silica with LiOH solution at a molar ratio of 1.5:1, separating the precipitate that forms at elevated temperature, and letting it cool, whereupon it liquefies to a polysilicate solution containing 23.4% SiO_2. Apparently the silicate that separates from hot solution is of higher ratio than that which remains (104). According to Patton and Cox (105), lithium silicates of molar ratios from 2:1 to 6.3:1 can be made in a similar manner at 75-150°C by leaving the precipitate in suspension and cooling to effect total solution. The polysilicate can also be made by dissolving silicon powder in LiOH solution at 50-80°C with $Cu(OH)_2$ present as a catalyst (106).
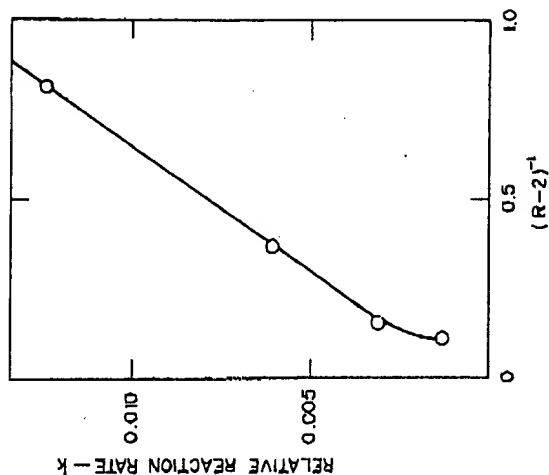
The presence of some lithium silicate in sodium or potassium silicate solutions is apparently of some advantage (107, 108).

Uses for Lithium Silicates and Polysilicates

A major use of polysilicates is in anti-corrosion coatings containing finely divided zinc, where the silica acts as an inorganic binder (109, 110). The addition of an organosiliconate improves the water resistance of the coating (111). A similar composition is said to provide a binder for brake linings (112). For a similar reason, a minor amount of a styrene–acrylic copolymer emulsion may be added, which also gives improved adhesion to steel (113). Another additive to improve saltwater resistance is a small percentage of barium hydroxide (114). Barium silicate is more soluble than the calcium or strontium salt and liberates enough silicate ion into solution to inhibit the corrosion of aluminum by alkali, according to Dupre and Booman (115). The adhesion and weldability of zinc-rich primers bonded with lithium polysilicate were improved by substituting some di-iron phosphide or cadmium for some of the zinc (116).

Some of the difficulties involved in using zinc-rich paints bonded with polysilicates were reviewed by Wright (117), who pointed out that in storage, slow reaction of zinc with the vehicle on aging reduced the quality of the final coating.
Several types of soluble silicates were evaluated, but a lithium polysilicate with

$SiO_2:Li_2O$ ratio about 5:1 was satisfactory, using zinc dust of 2–3 micron particle size. The advantage of lithium was mainly that the mixtures are more stable (118).

The binder properties are useful in other pigmented coatings such as clay-based paints (119). The zinc–lithium silicate coatings can be applied by anodic electrode-position on steel (120). In another type of use, lithium polysilicate provides an inter-mediate bond between the fluorocarbon polymer coating and metal on antisticking cook ware (121).

The precipitation of higher-ratio insoluble silicates from hot solution may be used to deposit siliceous coatings on hydrophilic surfaces. Sams (122) discloses that silica-rich coatings for optical or protective effects are deposited on surfaces such as glass from 2:1 ratio lithium silicate solution when the surface is immersed in the solution as it is heated to 95°C. Even after 10 sec, there is formed a colored film showing light interference, which must be of the order of 0.3 microns in thickness. Solutions with ratios from 1.3:1 to 10.7:1 may be used.

ORGANIC BASE SILICATES

Since silica dissolves above about pH 10.7–11.0, silicates can be prepared with organic bases having dissociation constants greater than about 10^{-3}, although some organic bases will dissolve in aqueous solutions of weaker bases with constants as low as 10^{-4} or 10^{-5} (123–125). Merrill and Spencer (124) reported the preparation of a number of water-soluble quaternary ammonium silicates by grinding silica gel with a solution of the free base. However, the compounds all appear to have a ratio of 2:1 when expressed as $SiO_2:(NR_4)_2O$ by analogy with the alkali metal system.

The unusual behavior of the $(CH_3)_4N^+$ ion in silica systems is probably due to its inability to form coordinate bonds with the oxygen of SiOH groups as sodium does at high concentration by exchanging one or more water molecules of the $(H_2O)_6Na^+$ ion for silanol oxygens. Hence the quaternary ammonium ion cannot act as a coordinative crosslinking agent to promote precipitation and gelling. Furthermore, there is some evidence that the quaternary ammonium ions are adsorbed on the surface of the silica, thus interfering with the dissolution and deposition of silica that is involved in particle growth.

In the case of the interaction of tetramethylammonium hydroxide with colloidal silica, there is evidence that, unlike NaOH, this quaternary ammonium base does not allow the colloidal and ionic species of silica to equilibrate readily. This is probably because the $(CH_3)_4N^+$ ions are strongly adsorbed on the surface of the colloidal particles and retard dissolution of $Si(OH)_4$. This was described by Beard (39), who examined mixtures of colloidal silicas with $(CH_3)_4N^+OH^-$(TMA) or NaOH with equivalent molar $SiO_2:Na_2O$ ratios from 0.5 to 3.25 by infrared spectroscopy. This method does not require diluting the sample or otherwise disturb-ing the equilibrium. Silica concentrations were 13.3, 15, and 20 wt. %. Mixtures were aged for up to 6 days to reach equilibrium.

Polymeric or colloidal species could be detected in sodium silicate solutions by an absorption band at about 1120 cm⁻¹. At a ratio of 2.0 a peak at about 1025 cm⁻¹ is assumed to be due to dimer, but is more likely $HSiO_3^-$. At a ratio of 0.67, where

silica must be present largely as SiO_3^{2-} ions, the characteristic peak is at about 980 cm⁻¹, whereas at a ratio of 1.0 it is not as sharp, suggesting the possible presence of some $HSiO_3^-$. With this interpretation, the results indicate that 3.25 or 1.0 ratio concentrated sodium silicate solutions contain only colloid and $HSiO_3^-$.

However, $(CH_3)_4N^+$ silicate solutions differ from the sodium silicate solutions in that even at 1.0 ratio, colloid still persists along with $HSiO_3^-$. Likewise, in 3.3 ratio solutions, there is much more colloid in the $(CH_3)_4N^+$ based solutions than with sodium base. The authors conclude that TMA cation "shifts the equilibrium to a mixture of low and high species." It is likely that the colloid phase is stabilized by an adsorbed monolayer of $(CH_3)_4N^+$.

It will be noted that in these experiments the solutions were made from TMA hydroxide and colloidal silica. It is possible that if TMA had been added to a dilute solution of polysilicic acid of low molecular weight at a ratio of 3.3 and then vacuum evaporated to 10% silica, solubility equilibrium would become established and the distribution of silica species would be like that in sodium silicate solutions.

The tetramethylammonium salt, $((CH_3)_4N)_8[Si_8O_{20}]$, was prepared and studied by Hoebbel and Wieker (126a), who converted the polysilicate ion to the trimethylsilyl derivative $[(CH_3)_3Si]_8[Si_8O_{20}]$ characterized by analysis and mass spectroscopy. This polysilicate ion is in effect a cube of SiO_2, indicating the possibility of small compact particles existing in sodium silicate solutions of $SiO_2:Na_2O$ ratio between 2:1 and 4:1. The copper-ammonium salt is discussed further in this chapter.

In crystalline organic base silicates, the size of the organic cation apparently controls the structure of the polysilicate anion. Hoebbel and Wieker (126b) prepared a crystalline tetra(n-butyl) ammonium silicate hydrate having the empirical composition 0.81 $N(n-C_4H_9)_4 \cdot SiO_2 \cdot 26.5H_2O$. The silica is present as two parallel five-membered siloxane rings held together by five oxygen bridges. Each silicon bears one ionizable OH group. However there are only four anionic charges on each five-membered siloxane ring; possibly there is a proton, H_3O^+, at the center of each ring. The corresponding $N(t-C_5H_{11})_4^+$ silicate has a similar structure.

A series of organic nitrogen base silicates, formulated as $(NRR'R''R''')_2O \cdot xSiO_2 \cdot yH_2O$, were patented in 1954 (127), where R, R', R'', are H, alkyl, aryl, aralkyl, hydroxylamino, and amino-substituted alkyl radicals, and R''' is any of the aforementioned groups (other than H, alkyl, or R'') or CH_2 groups forming part of a heterocyclic ring structure which includes the nitrogen. The value x varied from 0.5 to 4.0, and y from 0 to 15. Typical examples were $(HOC_2H_4)_4N^+OH^-$, $C_6H_5N(CH_3)_3^+OH^-$, and guanidines. A crystalline compound with analysis corresponding to the following formula was isolated:

$$C_6H_5N(CH_3)_3^+ \cdot HSiO_3^- \cdot 5H_2O$$
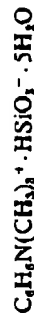
Quaternary alkanolammonium bases are desirable for making solutions of silicate free of alkali metals, since there is generally no amine odor and the compounds are very water soluble. Weldes patented a series of these materials along with a process for making them using ethylene oxide as follows, in water solution (128):
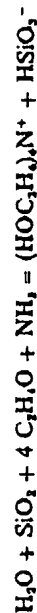
$$H_2O + SiO_2 + 4 C_2H_4O + NH_3 = (HOC_2H_4)_4N^+ + HSiO_3^-$$

Table 4.3. Properties of Commercial Silica Sols Listed by Manufacturer

Sol (Manufacturer)	Grade	SiO_2 (%)	Stabilizer Type	Stabilizer (%)	Ratio SiO_2:Na_2O	pH	Particle Diameter (nm)	Specific Surface ($m^2\,g^{-1}$)	Technical Bulletin
Ludox® (E. I. du Pont de Nemours & Co., Wilmington, Del.)	HS-40	40	Na_2O	0.41	95	9.7	12	230	E10260 (1976)
	HS-30	30	Na_2O	0.32	95	9.8	12	230	E10260 (1976)
	TM	50	Na_2O	0.21	240	9.0	21	130	E10260 (1976)
	SM	30	Na_2O	0.56	54	9.9	7	360	E10260 (1976)
	AS[a]	40	NH_3	—	—	9.0	21	130	E10260 (1976)
	LS	30	Na_2O	0.10	300	8.2	12	130	E10260 (1976)
	WP[b]	35	Na_2O	0.62	130	11.0	21	130	E08913 (1976)
	(AS)[f]	30	NH_3	—	—	9.6	13–14	210–230	A82273 (1974)
	AM[d]	30	Na_2O	0.13	230	9.0	15	210	A21163
Positively charged sols—Al_2O_3 coating									
	130M[c]	30	Cl	0.9	—	4.4	13–15	210	A85845 (1973)
	CL-X	46	—	—	—	9.1	—	—	E09550 (1976)
Nalcoag® (Nalco Chemical Co., Chicago, Ill.)	1115	15	Na_2O	0.8	19	10.4	4	750	K-1115
	(2326[f] / E136)	14.5	Na_2O	0.01	—	9.0	5	600	K-2326 (1975)
	1130	30	Na_2O	0.65	46	10.0	8	375	K-1030 (1976)
	1030	30	Na_2O	0.40	75	10.2	11–13	190–270	K-1140 (1972)
	1140	40	Na_2O	0.40	100	9.7	15	200	K-1050 (1976)
	1050	50	Na_2O	0.35	143	9.0	17–25	120–176	K-1034 (1972)
	1034A[g]	34			—	3.1	16–20	135–190	Data sheet (1974)
	(1129[h] / E-127)	30			—	3.5	16–25	150	
	(2325[i] / 43J25)	35			—	5	20	150	K-2325 (1975)
	(2327[j] / 41D01)	40	NH_3	0.10	—	9.3	20	150	K-2327 (1975)

Product	%	Stabilizer	%		pH	mμ		Reference
2600[k]	57	Na₂O	0.10	—	—	20	150	Data sheet (1973)
Nyacol® (Nyacol, Inc. Ashland, Mass.)								
1060	50	Na₂O	0.25	—	8.5	60	50	K-1060 (1975)
40D04[l]	50	—	—	—	4.0	16–22	—	
D2149[m]	30	NH₃	0.03	—	9.5	12–15	210	
D2361[n]	30	Al₂O₃	1.8	—	3.8	20	150	
215	15	Na₂O	0.75		11	3–4	—	Data supplied (1976)
830	30	Na₂O	0.45		10.7	8	—	
1430	30	Na₂O	0.35		10.4	14	—	
1440	40	Na₂O	0.48		10.4	14	—	
2050	50	Na₂O	0.48		10	20	—	
2034A°	34	—			3.5	20	—	
2046EC	46	Not given			9.8	20	—	
1430 NH₃	30	NH₃	0.2		9.4	13–15	—	
Snowtex® (Nissan Chem. Industries, Ltd., Tokyo, Japan; 200 Park Ave. New York)								
20	20	Na₂O	0.35	—	9.5–10	10–20	—	Data received (1977)
30	30	Na₂O	0.6	—	9.5–10.5	10–20	—	
C	20	Na₂O	0.2	—	8.5–9.0	10–20	—	
N[p]	20	Na₂O	0.04	—	9.0–10.0	10–20	—	
O[p]	20			—	3–4	10–20	—	
Syton® (Monsanto, Ltd. London, England)								
W15	15	Not given		—	9.8–10.6	36	75	No. 53-3 (E) M-E-2 (1975)
W30	30	Not given		—	9.8–10.6	36	75	
W50	50	Not given		—	9.8–10.6	36	75	
T15	15	Not given		—	9.6–10.2	18	150	
T30	30	Not given		—	9.6–10.2	18	150	
X30	30	Not given		—	9.6–10.2	111	250	
D30	30	Not given		—	9.5–10.0	8.5	325	
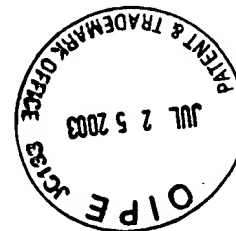
Table 4.3. (Continued)

Sol (Manufacturer)	Grade	SiO₂ (%)	Stabilizer Type	Stabilizer (%)	Ratio SiO₂:Na₂O	pH	Particle Diameter (nm)	Specific Surface (m² g⁻¹)	Technical Bulletin
Syton® (Monsanto Co. St. Louis, Mo.)					Sols no longer available				
	C-30	30	Not given		0.04	10.1	40	—	
	C-40	40	Not given		0.26	9.8	40	—	
	C-50	50	Not given		0.22	9.8	40	—	
	200	30	Not given		0.04	9.3	16	—	
	240	40	Not given		0.26	8.9	16	—	
	250	45	Not given		0.25	9.2	16	—	

[a] Sol contains 0.16% NH_3 and 0.08% Na_2O occluded within particles.
[b] The value for SiO_2 includes 0.6% Al_2O_3.
[c] An earlier type of AS differed in being more dilute, and of smaller particle size.
[d] Surface modified with aluminosilicate ions, 0.2% Al_2O_3.
[e] 30% solids comprised of 26% SiO_2, 4% Al_2O_3.
[f] Stabilized with ammonia (0.3%).
[g] Stabilized with acid only.
[h] Stabilized with acid in aqueous alcohol.
[i] Dispersed in dimethylformamide; pH at 50% dilution in H_2O.
[j] Stabilized with ammonia.
[k] Dispersed in oil (43%); fiber frictionizing.
[l] Dispersed in monoethyl ether of ethylene glycol (available in 1970).
[m] Stabilized with 0.25% NH_3 (available in 1970).
[n] Positively charged sol (available in 1970).
[o] Stabilized by acid only.
[p] Stabilizer not disclosed.